

is above the mean, indicating dissociation. The specific heat of these mixtures does not, however, show any corresponding alterations.

The author finally shows that if these propositions should prove to be an exposition of a general law, they will enable us to calculate the specific heat of one constituent of a mixture or solution, if we know the specific heat of the other constituent, the specific heat of the mixture, and the heat evolved or absorbed at two different temperatures between which these specific heats have been estimated. It may thus be possible to compare the specific heat of liquid and solid substances when both are placed under similar conditions, and relations may be discovered which at present are masked in consequence of the difference in the physical conditions of the substances to be compared.

II. "On Supersaturated Saline Solutions. Part III.—On a relation between the Surface-tension of Liquids and the Supersaturation of Saline Solutions." By CHARLES TOMLINSON, F.R.S., and G. VAN DER MENSBRUGGHE. Received April 6, 1872.

It was stated by one of us in Part II.\* that when a drop of a liquid is deposited on the surface of a supersaturated saline solution, it will do one of three things :—(1) mingle with the solution without any nuclear action ; (2) spread out into a film with powerful nuclear action ; or (3) assume the form of a lens, without any separation of salt. It was further stated that when a liquid forms a film or a lens, it does so according to the general proposition, that if a drop of a liquid B, with the surface-tension  $b$ , be placed on the surface of another liquid A, with the surface-tension  $a$ , the drop will spread into a film, if  $a > b + c$  ( $c$  being the tension of the common surface of the liquids A and B) ; but if, on the contrary,  $a = < b + c$ , the drop will remain in the form of a lens. Hence if B spread on A, A will not spread on the surface of B. When the liquids A and B mingle in all proportions,  $c$  has no value. The spreading of the drop may also be interfered with by the superficial viscosity of the solution, or the greater or less difficulty in displacing the superficial molecules.

It was also stated that if a greasy smear be made upon the clean interior surface of a flask above the solution, and the flask be inclined so as to bring a portion of the solution against such smear, the liquid does one of two things :—(1) it breaks up into well-defined globules, which roll over the smear without loss of tension, in which case the smear has no nuclear action ; or (2) as soon as the solution reaches the smear its edge flattens and becomes ragged, in which case the smear is nuclear and the salt separates.

A glass rod drawn through the hand becomes covered with a smear or film ; or the same rod, by exposure to the air, contracts a film by the

\* Philosophical Transactions for 1871, p. 52.

condensation of floating vapour, or a deposit of film-forming dust, and so is brought into the nuclear condition.

It was further stated that when a lens of oil is resting on the surface of a solution, the flask may be rapidly rotated or briskly shaken, so as to break up the oil-lens into a multitude of minute globules, giving the solution the appearance of an emulsion; but that by repose the solution regains much of its transparency, without any separation of salt; but that if, while the flask is being turned round, a sudden jerk be given to it, so as to flatten some of the globules against the side, the solution instantly becomes solid.

The powerful action of films in putting an end to the state of supersaturation being thus established, it occurred to one of us, who had already succeeded in explaining a number of obscure phenomena on the principle of surface-tension\*, that that force, properly handled, would suffice to account for most, if not all, the varied phenomena of supersaturation. According to this view, whatever tends greatly to lower the surface-tension of a supersaturated saline solution, causes a separation of salt, and at once puts an end to the condition of supersaturation.

In order to test this view, a large number of experiments have been performed by one of us during the last six months, consisting of repetitions of former experiments or of new ones suggested by one or both of us. All these experiments have been performed in the open air at Highgate, near London, the object being to avoid all possible miscarriage from the effects of floating dust in the air of a room. It had been suggested that some of the former results as to the action of films might have been vitiated from this source; and although this does not appear to have been the case, yet it is with much satisfaction that the experimenter refers to the greater facility and certainty with which experiments of this kind are conducted in the open air, as compared with those made in a room. In the open air a gentle wind would sometimes blow over the mouths of the flasks, sufficient to produce a low musical note, without any nuclear action, unless a speck of soot or a small insect were carried into the solution; but in general, in order to prevent evaporation, the flasks were kept covered with watch-glasses or small beakers, except when performing an experiment.

The salt used in the following experiments was sulphate of soda, in large crystals, not effloresced, one of three strengths being adopted as circumstances required, and which will be indicated when necessary, namely, 1 part of salt to 1 of water, 2 parts of salt to 1 of water, and 3 parts of salt to 1 of water. Every solution was first made in a large flask, and filtered boiling into eight or ten small flasks, which were reboiled, covered with watch-glasses or beakers, and carried on a tray into the open air. The same experiment was repeated on a number of these solutions of the same strength.

\* "Sur la Tension superficielle des Liquides," par Gt. Van der Mensbrugghe, Répétiteur à l'Université de Gand. Mémoires couronnés par l'Acad. Royale de Belgique, tome xxxiv. 1869. See also Phil. Mag. for Dec. 1869 and Jan. 1870.

The points to which this experimental inquiry tended are included in the four following propositions:—

I. That a supersaturated saline solution contained in a catharized flask will remain liquid so long as its free surface, or the surface in contact with the sides of the flask, does not undergo in one or many points a notable diminution of surface-tension.

II. That if we deposit on the surface of a supersaturated saline solution a drop of a liquid of feeble tension, it spreads, and crystallization takes place immediately or after a short time.

III. That while a liquid of feeble tension produces crystallization after a time more or less short, a liquid of considerable contractile force (such as pure water) not acting chemically on the solution, may be brought into contact with it without producing change of state.

IV. That as a liquid of feeble tension produces crystallization, so a solid covered more or less with a film of such liquid produces change of state, either at once or after a short time.

But before any conclusions could be drawn from the results of experiments as to the relation between the surface-tension of liquids and the state of supersaturation in saline solutions, it was necessary to measure the surface-tension of the solutions of Glauber's salt operated on. Accordingly the following data were determined, *first*, for a solution containing 1 part of salt to 1 of water, and, *secondly*, for a solution containing 2 parts of salt to 1 of water. The diameter of the capillary tube was 1.598 millim.\*

Specific gravity of the solution 1 salt to 1 water at  $17^{\circ}\text{C.} = 1.198$ .

The capillary height 11 millims.

The specific gravity of the other solution = 1.289.

The capillary height 8.7 millims.

These data give, according to the formula  $t = \frac{r \cdot h \cdot d}{2}$  (in which  $t$  is the tension,  $h$  the height,  $d$  the density, and  $r$  the radius of the tube), for the superficial tensions of the solutions in question, not a greater value than from 4 to 5.2.

If the states of supersaturation of saline solutions depend on the maintenance of surface-tension, according to the first proposition, any force or substance that produces a notable diminution of such tension will cause the state of supersaturation to cease.

Such a force is heat, while such substances as camphor, benzoic acid, &c. have a marked effect in lowering the superficial tension of water, and in doing so undergo those remarkable gyrations which are so well known.

And first with respect to heat, applied, not so as to affect the whole solution, but locally, so as to raise the temperature at one part or point of the surface, while the other parts remained at the temperature of the atmosphere.

\* The tube was calibrated by Dr. E. J. Mills, F.C.S. &c.

*Experiment 1.* Four flasks, each about half full of a supersaturated solution of Glauber's salt (2 salt to 1 water), were exposed to a temperature of 32° F. for an hour. A red-hot poker was then passed down the neck of each flask, and in two of them the hot metal was brought into contact with the surface of the solution so as to raise a volume of vapour. There was no separation of salt in any one case.

*Experiment 2.* A solution containing a considerable mass of the seven-atom salt at the bottom of the flask was moved over the flame of a spirit-lamp in a line from the bottom of the flask to the neck, so as to heat one part only of the flask. The only effect was to convert a portion of the surface of the seven-atom salt into the anhydrous; but there was no crystallization. After some hours the anhydrous portion had again taken up its water of crystallization.

*Experiment 3.* A solution of 2 salt to 1 water that had been in the open air during twenty-four hours was uncovered, and water nearly boiling was dropped upon it. A slight cloudiness came over the solution, but there was no crystallization.

Next day a very weak solution of Glauber's salt nearly boiling was dropped upon the surface with no nuclear action.

*Experiment 4.* An eight-ounce globular flask had the globe filled with a solution of 2 salt to 1 water. Solutions of two different strengths, namely 1 salt to 1 water, and 3 salt to 1 water, at a nearly boiling temperature, were dropped upon it, but with no nuclear action.

*Experiment 5.* A solution of 1 salt to 1 water had filtered into it a nearly boiling solution of 3 salt to 1 water. The drops descended to the bottom of the flask in beautiful rolling rings, but there was no nuclear action.

*Experiment 6.* The neck of a flask was inclined over the flame of a spirit-lamp, so as to boil the upper part of the solution, while the lower part remained cold. Water was driven off in vapour, so as to leave a crust of salt in the neck. This, when the flask was left to itself, gradually absorbed moisture and trickled down, and was also washed down into the solution; but there was no nuclear action either from this or from the heat.

These experiments on the action of heat lead to the conclusion that, however much it may diminish the superficial tension of the solutions, it does not apparently disturb the state of supersaturation. This result may be explained with reference to the feeble tension of the solution ( $=4$ ), and to the fact that heat locally applied does not greatly diminish it. Moreover, heat tends to oppose crystallization by increasing the solubility.

Numerous experiments were tried as to the action of newly sublimed camphor and benzoic acid on the solutions. The flasks containing these bodies floating on the solutions were plugged with cotton-wool and kept for some months, during which time they were repeatedly shaken; but there was no separation of salt. The camphor and benzoic acid formed weak solutions with the supersaturated solutions; but the tension of camphorated

water being  $\approx 4.5$ , and that of an aqueous solution of benzoic acid falling within the limits 4 and  $5.2$ , the difference in tension is too small to produce a rupture of equilibrium. The same remark applies to a solution of soap and of bicarbonate of soda, which had no nuclear action.

*Action of Vapours.*—It has been shown by recent researches that the presence of vapours in the air of a room, even in minute quantity, has a marked influence in lowering the tension of water and other liquids, so as to account for the discordant values of various careful measurements of the capillary heights of such liquids. As to the nuclear action of the vapours of certain volatile liquids upon supersaturated saline solutions, many observations had been made by one of us, leading to the conclusion that such vapours are strongly nuclear when they become condensed into the form of films on the surface of the solutions, as when the latter is of a lower temperature than the former. In order to ascertain whether vapours, as such, that is, without forming films, have any nuclear action, the following experiments were contrived. The vapour was presented to the surface of the solution by means of a bit of sponge tied to the end of a glass rod, wetted with the volatile liquid and carefully passed down the neck of each flask, so as to avoid touching the side, and bringing the sponge close upon the surface to avoid touching that also\*. The sponge was held over the solution several minutes, then carefully withdrawn and the flasks covered, leaving the interior charged with vapour. The liquids used were ether, absolute alcohol, chloroform, bisulphide of carbon, wood-spirit, and benzole. The solutions were of all three strengths, and the temperature from  $40^{\circ}$  to  $47^{\circ}$  F. After many hours and even days the flasks had a strong odour of the vapours in question, but there was no separation of salt.

Vapour of camphor was also tried in the following manner :—

*Experiment 7.* A quantity of camphor was placed in a small retort, the beak of which, made chemically clean by being heated in the flame of a spirit-lamp, was passed into a flask containing a solution of 2 parts salt to 1 of water. The camphor in the belly of the retort was then boiled so as to produce a powerful jet of vapour upon the surface of the solution. The camphor condensed upon such surface in the form of a fine white powder without any nuclear action.

In this case a portion of the vapour of camphor or of the powder would dissolve in the solution without producing in it a notable diminution of surface-tension. The same remark applies to the other vapours, to the action of solid camphor and benzoic acid, of heat, &c.

So also, as stated in Part II., glycerine mingles with the solution without any nuclear action. Now the surface-tension of glycerine  $\approx 4.2$ ; so that it can have no effect in lowering the surface-tension of a solution  $\approx 4$ , and does

\* In a few cases the wet sponge did touch the solution for an instant, so as to take up a small portion, which immediately crystallized upon the sponge; but the crystallization thus produced, not being in contact with the solution, the latter retained its liquid state.

not sufficiently lower the tension of a solution  $=5.2$  to produce a rupture of equilibrium.

It was also stated that bisulphide of carbon  $t=3.3$  to  $3.5$ , and chloroform  $=2.98$  to  $3.12$ , formed lenses on the surface of the solution, and that on gently agitating the flask they fell to the bottom, where they remained permanently without any nuclear action. Creosote  $=3$  behaves in the same manner. Now, in any one of these cases, the tension  $t+c$  must be greater than  $4.5$ , and hence there can be no separation of the salt.

We now pass on to consider the second proposition, namely, that if on the surface of a supersaturated saline solution there be deposited a drop of a liquid of feeble tension, the drop spreads and crystallization is determined. Now it is shown in Part II. that drops of ether, of alcohol, and of similar volatile liquids, as well as of certain oils, both volatile and fixed, spread over the surface of the solutions and act as powerful nuclei. On the surface-tension theory, a liquid such as ether, of which the tension  $=1.88$ , or alcohol  $=2.5$ , or wood-naphtha  $=2.11$ , or oil of lavender  $=2.9$ , must spread on the surface of a supersaturated solution of Glauber's salt of which the surface-tension is as high as from  $4$  to  $5.2$ . This is true in a large number of cases that have been observed, and so far the phenomena are consistent with the theory; but there are cases in which liquids of low tension, such as oil of turpentine  $=2.2$  to  $2.4$ , and some varieties of castor-oil  $=2.5$ , do not form films, but well-shaped lenses, and remain as such during many hours and even days. Quincke seems to have met with cases of this sort in his elaborate inquiry on the capillary phenomena of the common surface of two liquids\*; and he endeavours to account for these exceptions to the general law by the statement that if a lens-shaped drop of a liquid 2 (of low tension) remain on the free surface of a liquid 1 (of much higher tension) without spreading itself out, then it is certain that in most, and probable that in all cases the free surface of liquid 1 is rendered impure by a thin layer of a foreign liquid 3. Now in experiments on supersaturated saline solutions, the flasks, the filtering-apparatus, and the solutions must be, as already explained by one of us, chemically clean; so that in boiling and filtering a solution into clean flasks in which it is boiled up again, covered over, and left to cool in the open air of the country, it is difficult to imagine the existence of such a film as M. Quincke refers to. Moreover, did such a film exist, the solution in cooling would probably become solid under its action. Indeed this sometimes happens in the case of flasks that have been already used in experiments on the nuclear action of oils; for, however carefully they are cleansed, it may happen that one or two out of a dozen may not be quite clean, so that, in the cooling of a boiling solution, a film detached from the walls of the flask may spread over the surface with nuclear action. In order, if possible, to prevent the formation of such a film, the following experiment was made:—

*Experiment 8.* A solution of 1 part of Glauber's salt to 1 of water,

\* Poggendorff's Annalen, vol. cxxxix. See also Phil. Mag. for April 1871.

with the addition of a bit of caustic potash, was boiled and filtered into four clean flasks. When cold, a drop of castor-oil was deposited upon the surface of each of the solutions. It flattened at first, but soon recovered the lenticular form. There was no nuclear action during an hour. On gently shaking the flasks, the oil was diffused through the solution without nuclear action.

In an experiment described in Part II. fragments of stearine were scraped into a solution with immediate nuclear action. In such a case, the stearine furnished the film-forming material that produced the solidification of the solution. The solution was boiled with the stearine in it; and in cooling the stearine formed into solid disks without nuclear action, although the flask was frequently shaken. In this case the boiling solution had saponified or otherwise removed the film-forming matter, or, in other words, had made the stearine chemically clean.

There is also a difficulty in the case of oil of turpentine, as in the following experiment :—

*Experiment 9.* A drop of an old but clear and bright oil of turpentine was deposited on the surface of a solution containing 2 parts of salt to 1 of water. The drop flashed out into a film, and the solution immediately became solid. The turpentine was now distilled, and a drop of the distillate was deposited on a similar solution, when it formed a well-shaped lens with no nuclear action, although the flasks were left out during several days.

Now the tension of the old oil first used is  $\approx 2.2$ , and had the effect of distillation been greatly to exalt the tension, the experiment would have been intelligible according to the theory; but on measuring it the tension was found to be only 2.4.

A somewhat similar case is given in Part II., in which an old oil of bitter almonds was strongly nuclear, while the same oil freshly distilled had no such action, but became converted into benzoic acid, still without any separation of salt. After some days, to prove that the solution was still supersaturated, it was touched with an unclean wire and it immediately became solid.

Still, however, there are such a large number of cases in which oils and other liquids spread upon the surface of the solutions with nuclear action as to justify the labour bestowed upon the theory by one of us during the last six months. Many of these cases are stated in Part II.; but a few of them may be repeated here for the sake of comparing the action of such liquids upon solutions of different strengths, which was not done before.

If we take a number of oils, the tension of which varies from about 2.5 to 3.5, a drop of any one of them, according to the theory, ought to spread on the surface of a solution where  $t = 5.2$ , and not in all cases spread on the solution of which  $t = 4$ .

*Experiment 10.* Twelve flasks, containing a solution of 1 part salt to 1 of water were prepared, and a drop of each of the following oils formed

films with immediate crystallization of the solutions, viz. pale seal-oil, sperm-oil, cotton-seed oil, and niger-oil. A drop of linseed-oil formed a lens; but this soon becoming ragged, crystals diverged from it. A drop of castor-oil formed a lens with no nuclear action.

*Experiment 11.* Three of the above solidified solutions were heated over a lamp, boiled and covered over. The oil collected on the surface in innumerable small disks. Next morning one of the solutions was found crystallized, and the other two became solid on gently agitating the flasks.

In this case as the solutions cooled down or were gently agitated the disks spread out into films with nuclear action.

*Experiment 12.* A solution of 3 parts salt to 1 of water was filtered into twelve flasks, when a drop of each of the following oils deposited on the surfaces of the solutions became lenticular without any separation of salt, viz. pale seal-oil, olive-oil, rape, castor-oil, croton-oil, niger, sperm, and cotton-seed oil.

So far this result is in accordance with the theory.

*Experiment 13.* A solution of the same strength as in the last experiment was employed, when a drop of seal-oil, sperm, cotton-seed, and niger spread out into films with powerful nuclear action. Linseed- and castor-oil formed lenses with no such action.

Now it must be remarked that on the day when Exp. 12 was made the weather was dull, damp, and cloudy, and during the time of Exp. 13 the weather was bright and clear. Some years ago it was a matter of frequent observation to one of us, that the formation of cohesion-figures on the surface of water was much more rapid and decisive, with altogether finer and sharper results, in bright weather as compared with dull, damp, wet, or foggy weather. The same remark applies to the motions of camphor on water, and to those curious phenomena known as "camphor-currents" and "camphor-pulsations"\*. In the production of all these phenomena, as has been shown by one of us†, surface-tension plays a most important part; and such tension is lowered in dull foggy weather probably by the condensation of the vapour of volatile matters contained in the atmosphere. A drop of a liquid under such conditions may not spread on the surface of water or of mercury, the latter being especially liable to such influences; whereas on a bright day such surfaces are particularly active, and experiments succeed which some hours or days before failed to produce the results expected.

Then, again, as pointed out by one of us in Part II., the viscosity of the surface, or of the drop of liquid placed upon it, may greatly interfere with the operation of the law by which a liquid B spreads upon the surface A. A supersaturated saline solution has a considerable viscosity of surface, which it retains for many hours after it has cooled down. In the course of about twenty-four hours the more watery particles come up to the sur-

\* Phil. Mag. for Dec. 1869.

† Sur la Tension superficielle des Liquides, par G. Van der Mensbrugghe.



face and the tension improves ; so that the same surface which may have sufficient tensile force to cause a drop of oil to spread upon it, might some hours earlier have retained it in the lenticular form\*.

There are also certain modifications to which oils &c. are subject in consequence of the presence of ozone and other matters in the air, which may somewhat disturb the results expected to be obtained from the action of surface-tension.

It was stated in Part II. that when an oil &c. assumes the lenticular form, the solution may be agitated so as to break up the lens into a multitude of globules, and give the solution the appearance of an emulsion. In such a case the tensions of the two liquids are of nearly the same value ; if not, the agitation often produces crystallization ; but even in the former case it was stated that a sudden jerk will sometimes produce immediate solidification of the solution. Now taking the tension of the solution at 5·2, and that of oil of olives at 3·7, and the tension at the surface of separation of the solution and the oil-lens at about 2, then the sum  $3\cdot7 + 2$  is equal to the tension of the solution, and the spreading on the surface ought to be impossible, unless fine clear weather, absolutely clean vessels and solutions, and the absence of surface-viscosity concur to increase the surface-tension of the solution. At the surface of separation of the solution and of the glass, spreading may be possible in the case of certain oils without these concurring circumstances. Suppose a drop or a minute globule of oil to be brought into direct contact with the wet solid side of the solution, as by the jerk above referred to, the film of solution is displaced and the oil can wet the solid side. It may happen that the tension  $t$  of the solution at the wall of the flask is greater than the sum of the tension  $t$  of the surface of separation of the solution and of the oil, plus the tension of the oil in contact with the solid side ; that being the case, the instant solidification consequent on the jerk is accounted for.

It will be seen, then, that when the drop of oil &c. remains as a lens on the surface, there is a diminution of tension at the surface of the solution in contact with the oil ; but in such a case the tension is not sufficiently lowered at one point as to render molecular equilibrium impossible at this point, and so break up the whole system of supersaturation. But if the solution be agitated, so as to bring into contact with the surface of the glass a portion of the drop, there will still be diminution of tension at the surface of the solution in contact with the solid, and now the diminution is sufficient to produce crystallization. Thus it appears that oils may act

\* Some of the distinguished physicists who are now engaged in studying the phenomena of surface-tension refer to the embarrassing effects of surface-viscosity. Thus Herr Lüdige remarks that a solution of soap ( $t=2\cdot8$  to 3) does not spread upon a solution of Panama-wood ( $t=5\cdot7$ ) ; and it has been shown by one of us that the viscosity of the surface explains why a solution of soap does not spread on a solution of saponine or of albumen ; and, on the other hand, the liquid drop being viscous, there is no extension, or only a feeble one, since the slight difference in tension is equilibrated by the resistance of the viscous liquid.

differently according as they alter the tension of the liquid freely exposed to the air, or the tension of the liquid in contact with the glass, which is not of the same value.

With respect to Proposition III. there is no difficulty. A liquid of considerable contractile force, such as pure water, produces no separation of salt in a solution of less contractile force. This explains a number of cases described in a note by one of us submitted to the Society in July last\*, in which solutions exposed for hours together to heavy rain did not crystallize, unless the rain brought down a speck of soot or some unclean body that lowered the surface-tension of the solution. Indeed we know of no liquid of superior tensile force to that of the solution, and not acting chemically upon it, that has any influence in producing crystallization.

Proposition IV. also agrees with the phenomena. A glass rod or other solid, more or less smeared with a film of a liquid of low tension, when brought into contact with the solution determines crystallization by lowering the surface-tension. Such, then, is the function of a nucleus with respect to supersaturated saline solutions. If the solid be made chemically clean, it may be plunged into the solution without altering its tension, and hence there is no separation of salt. And here it may be remarked that such a case is possible that a crystal of the salt itself may be brought into contact with the solution without disturbing its tension, and hence be inactive. It has never been pretended that a crystal of the salt is not a good nucleus for a supersaturated solution of its own kind; all that has been stated by one of us is that, under special conditions, such a crystal may be lowered into the solution without acting as a nucleus.

III. "Remarks on the Sense of Sight in Birds, accompanied by a description of the Eye, and particularly of the Ciliary Muscle, in three species of the Order *Rapaces*." By ROBERT JAMES LEE, M.A., M.D. Communicated by ROBERT LEE, M.D., F.R.S. Received April 11, 1872.

It is proposed in this communication to describe certain peculiarities in the eye of the bird as compared with the eyes of other vertebrata; and further to examine to what extent those peculiarities enable us to explain the remarkable powers of sight with which all species of birds are more or less highly endowed.

Those who study the habits and modes of existence of the lower animals, find great interest in applying to various phenomena connected with them the results of anatomical investigation, and in endeavouring to discover such causes, or means adequate to produce such effects, as to render the supposition of the existence of an indefinite property like instinct very frequently unnecessary.

This method it is my desire to apply in the explanation of those high

\* *Suprà*, p. 41.